

Supporting Information

Efficient Solid State Dye-Sensitized Solar Cells Based on An Oligomer Hole Transport Material and An Organic Dye

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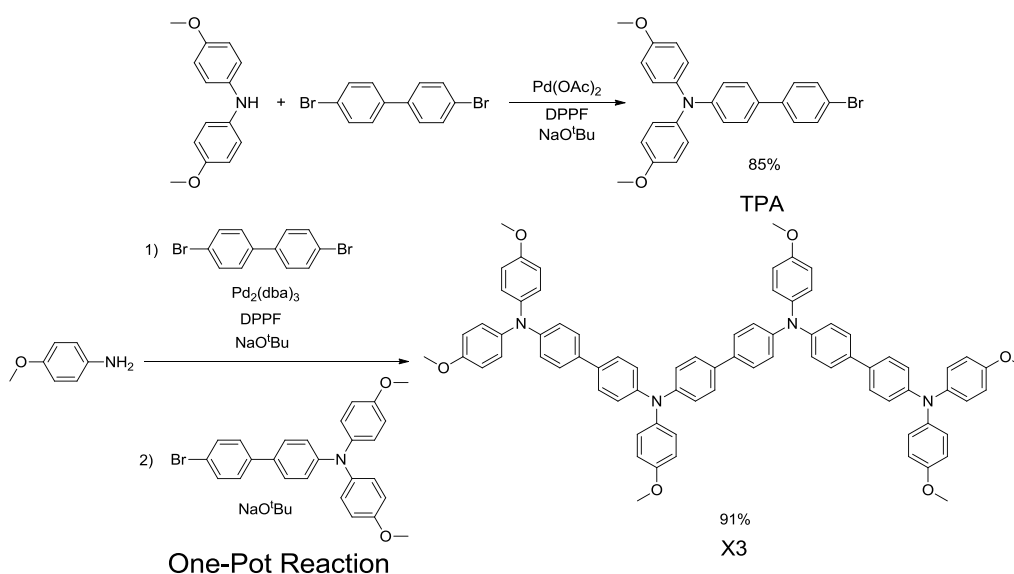
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Experimental

General methodology. Solvents were dried by standard procedures. All other chemicals were purchased from Sigma-Aldrich (Sweden) and used without further purification. Dye LEG4 bought from Dyenamo, Z907 purchased from Solaronix. NMR spectra were measured on Bruker AVANCE 500 MHz spectrometer. HRMS were performed using a Waters (USA) MALDI micro MX Matrix assisted laser desorption ionization-time of flight mass spectrometer. Electrochemical experiments were performed using a CH Instruments electrochemical workstation (model 660A). The measurements were carried out at room temperature with a conventional three-electrode configuration consisting of glassy carbon working electrode, a platinum wire counter electrode and a nonaqueous Ag/AgNO₃ reference electrode. The potentials are quoted against the ferrocene internal standard.

Synthetic Route:



Scheme S1. Synthesis route of X3

4'-bromo-N,N-bis(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine (TPA) ^[1].

A mixture of 4,4'-dibromo-1,1'-biphenyl (3.76 g, 12.0 mmol), Pd(OAc)₂ (18.0 mg, 0.08 mmol), DPPF (88.7 mg, 0.16 mmol), bis(4-methoxyphenyl)amine (0.92 g, 4.0 mmol), and sodium tert-butoxide (0.58 g, 6.0 mmol) in dry toluene (25 ml) was placed in a three-necked flask under a nitrogen atmosphere and stirred at 100 °C for overnight. After cooling, the reaction was quenched by adding water, and then the reaction solution was extracted with ethyl acetate. The organic layer was dried over anhydrous Mg₂SO₄ and evaporated under vacuum. The product was purified by silica gel column chromatography (hexane/EtOAc, 5:1). White solid of **TPA** was obtained in 85 % yield (1.56 g). ¹H NMR (DMSO-d₆, 500 MHz, 298 K), δ (ppm): 7.66 (d, 4H, J = 5.0 Hz), 7.50 (d, 2H, J = 5.0 Hz), 7.09 (d, 4H, J = 10.0 Hz), 6.93 (d, 4H, J = 10.0 Hz), 6.91 (d, 2H, J = 10.0 Hz), 3.80 (s, 6H); ¹³C NMR (C₆D₆, 500 MHz, 298 K), δ (ppm): d 148.01, 145.05, 139.88, 132.89, 132.71, 131.86, 130.08, 128.56, 127.42, 124.95, 122.73, 120.91, 55.04. MS (ESI): Positive ion: m/z=460.08 [M+H]⁺, calculated 460.08.

Synthesis of N₄,N₄'-([1,1'-biphenyl]-4,4'-diyl)bis(N₄,N₄',N₄'-tris(4-methoxyphenyl)-[1,1'-biphenyl]-4,4'-diamine (X3).

Using one-pot reaction^[2], to a solution of Pd₂(dba)₃ (6.2 mg, 0.06 mmol), and DPPF (5.5 mg, 0.1 mmol), in toluene (10 mL) under nitrogen atmosphere was added 4,4'-dibromo-1,1'-biphenyl (312 mg, 1.00 mmol) at room temperature, and the resultant mixture was stirred at that temperature for 10 min. Then, sodium tert-butoxide (240 mg, 2.50 mmol) and 4-methoxyaniline (246 mg, 2.00 mmol) were added to this solution and stirred at 90 °C for 8 h. At this time, the starting materials had disappeared as judged by TLC. To this solution was added an additional amount of sodium tert-butoxide (240 mg, 2.50 mmol) followed by 4'-bromo-N,N-bis(4-methoxyphenyl)-[1,1'-biphenyl]-4-amine (**TPA**) (921.0 mg, 2.00 mmol), and toluene (10 mL). The resultant reaction mixture was stirred at 100 °C for overnight. After cooling, the reaction was quenched by adding water, and then was extracted with ethyl acetate. The organic layer was dried over anhydrous Mg₂SO₄ and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (hexane/EtOAc, v/v, 3:1) to give X3 as pale yellow solid (1050 mg, yield 91 %). ¹H NMR (d₆-DMSO, 500 MHz, 298 K), δ (ppm): 7.51 (d, 4 H, J = 5.0 Hz), 7.48 (d, 4 H, J = 10.0 Hz), 7.44 (d, 4 H, J = 5.0 Hz), 7.06 (d, 4 H, J = 15.0 Hz), 7.01 (d, 8 H, J = 10.0 Hz), 6.99-6.94(m, 12 H), 6.91 (d, 4 H, J = 10.0 Hz), 6.80 (d, 4 H, J = 10.0 Hz), 3.75 (s, 6 H), 3.73 (s, 12 H); ¹³C NMR (C₆D₆, 500 MHz, 298 K), δ (ppm): 156.93, 156.49, 148.35, 147.57, 147.33, 141.64, 141.14, 135.22, 134.87, 133.68, 128.35, 127.96, 127.76, 127.67, 126.90, 123.89, 121.88, 115.30, 115.19, 55.05. TOF-MS: Positive ion: m/z=1156.4905 [M+H]⁺, calculated 1156.4982.

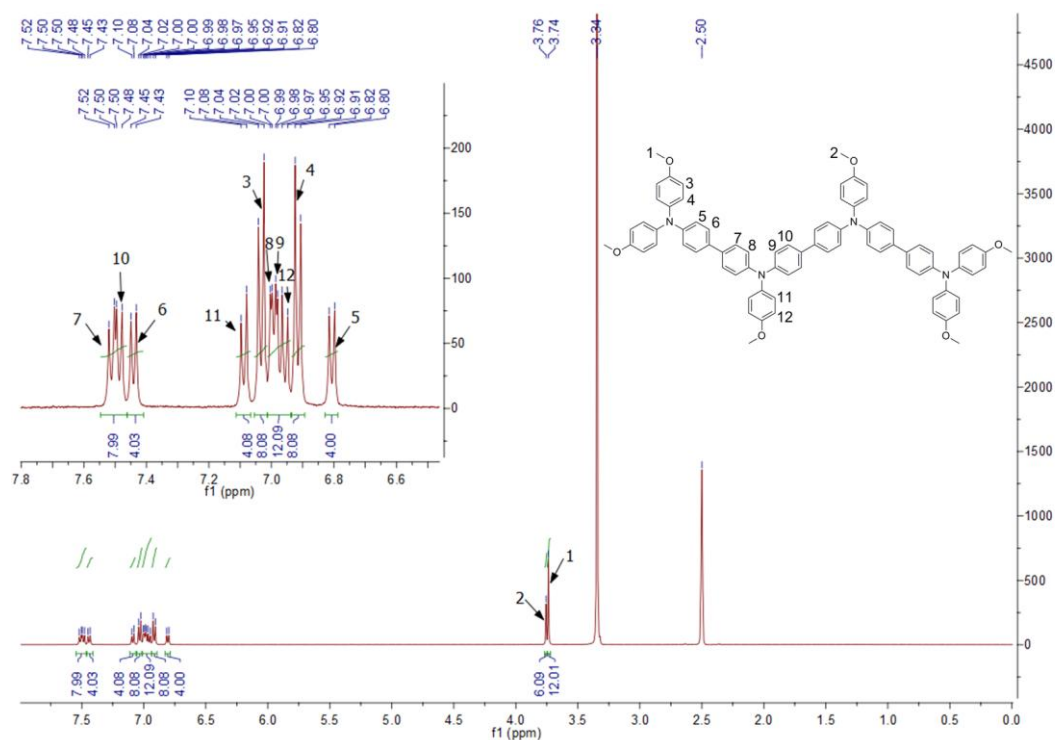


Figure S1. ^1H NMR (DMSO- d_6) spectrum of X3

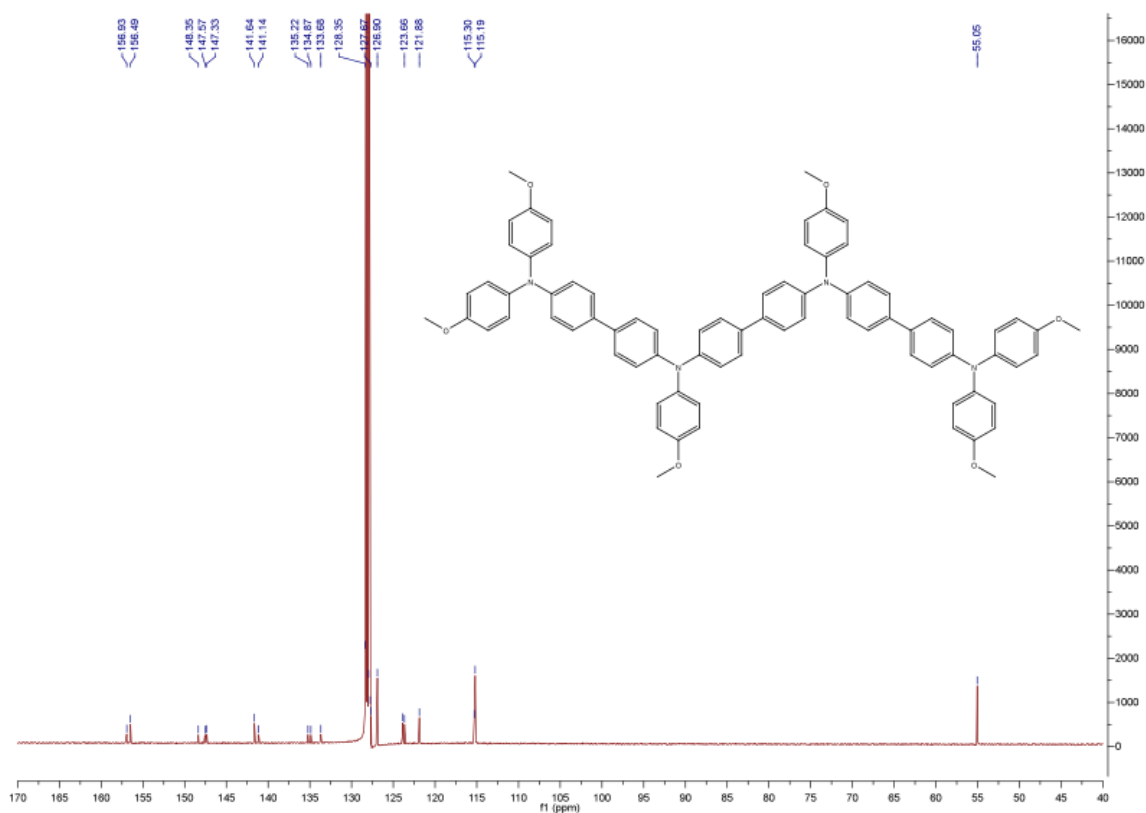


Figure S2. ^{13}C NMR (C_6D_6) spectrum of X3

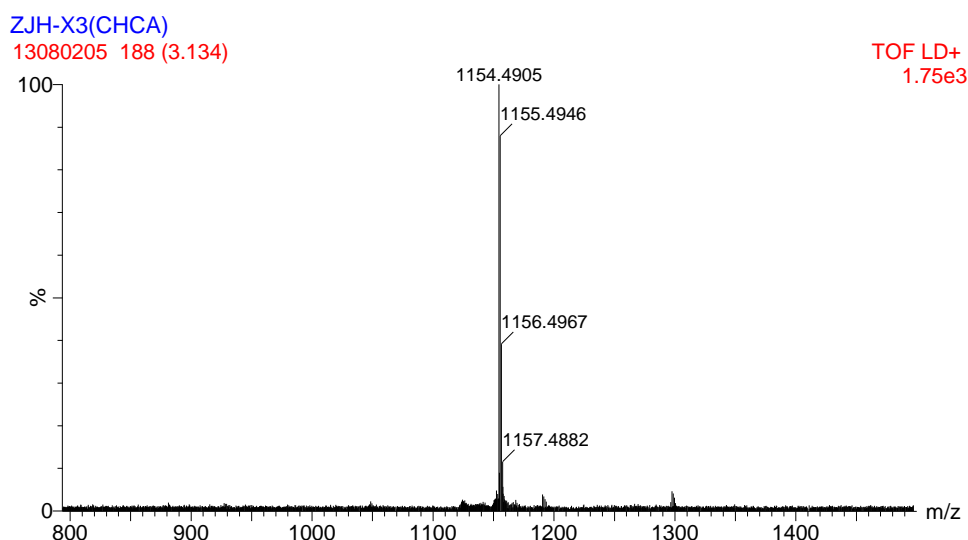


Figure S3. HR-MS spectrum of X3

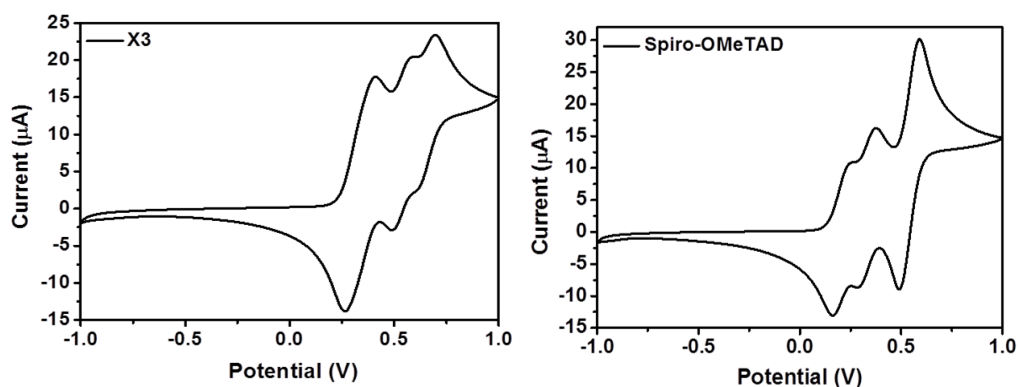


Figure S4. Cyclic voltammograms of X3 and Spiro-OMeTAD vs. Ag/AgNO₃ electrode.

Table S1. Summary of the electrochemical and molecular weight of the HTMs used in this study.

HTMs	$E_{\text{ox}}(\text{V})^{[a]}$ vs NHE	HOMO (eV) ^[b]	LUMO (eV)	E_{gap} (eV)	Molecular Weight
X3	0.77	-5.24	-2.32	2.92	1155.4
Spiro-OMeTAD	0.63	-5.10	-2.20	2.90	1225.4

[a] Measured in a dichloromethane solution containing 0.1 M of tetrabutylammonium hexafluorophosphate, n-Bu₄NPF₆ in a three-electrode cell, where the Ag/AgNO₃ electrode (acetonitrile as solvent) was used as the reference electrode, glassy carbon disk as the working electrode and platinum wire as the counter electrode. Scan Rates: 50 mV/s. Each measurement was calibrated with Fc. $E_{1/2}^{\text{Fc}} = 0.20$ V. [b] HOMO = $-5.1 - (E_{1/2}^{\text{Fc}} - E_{1/2}^{\text{Fc}})^{[3]}$, LUMO = HOMO - E_{gap}

Device Fabrication ^[4]

Fluorine-doped tin-oxide (FTO) coated glass substrates were patterned by etching with zinc powder and 2 M hydrochloric acid. A compact TiO₂ blocking layer was first deposited onto the surface of a pre-cleaned

FTO substrate by spray pyrolysis on a hotplate at 500 °C using an airbrush. The solution used in the spray pyrolysis was 0.2 M Ti-isopropoxide, 2 M acetylacetone in isopropanol. 10 spray cycles were used as standard parameter. Nanoporous TiO₂ films were coated on the compact TiO₂ layer by screen-printing a colloidal TiO₂ paste (Dyesol DSL 18NR-T). The thickness of the film is ca. 2.0 μm, as measured with a DekTak profilometer. After sintering the TiO₂ film on a hotplate at 500 °C for 30 min, the film was cooled to room temperature and immersed in 0.02 M aqueous TiCl₄ at 70 °C for 30 min. The film was then rinsed by deionized water and then annealed on a hotplate at 500 °C for 30 min. After cooling to 90 °C, the film was immersed for 2 h in 0.2 mM solution of LEG4 dissolved in tert-butanol and acetonitrile (1:1); then the sensitized electrodes were rinsed by ethanol and dried; Subsequently, the chlorobenzene solution containing corresponding HTM and additives was applied to form the HTM film by leaving the solution to penetrate into the sensitized electrode for 30 s and then spin-coating for 30 s with 2000 rpm. After cells were left in the dark in air overnight, the 200 nm thick Ag back contact was deposited onto the organic semiconductor by thermal evaporation in a vacuum chamber (Leica EM MED020) with a base pressure of about 10⁻⁵ mbar, to complete the device fabrication.

Device Characterization

Current-Voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a Keithley model 2400 digital source meter. The light source was a 300 W collimated xenon lamp (Newport) calibrated with the light intensity to 100 mW•cm⁻² at AM 1.5 G solar light condition by a certified silicon solar cell (Fraunhofer ISE). IPCE spectra were recorded on a computer-controlled setup comprised of a xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a potentiostat (EG&G PAR 273). The setup was calibrated with a certified silicon solar cell (Fraunhofer ISE) prior to measurements. All ssDSC samples were illuminated from the glass side with an aperture area of 0.20 cm² (0.4×0.5 cm²). The prepared ssDSC samples were masked during the measurement with an aperture area of 0.20 cm² (0.4×0.5 cm²) exposed under illumination. Electron lifetime was measured by the custom-made “toolbox setup” using a green-light-emitting diode (Luxeon K2 star 5 W, λ_{max}=530 nm) as light source to provide the base light intensity.

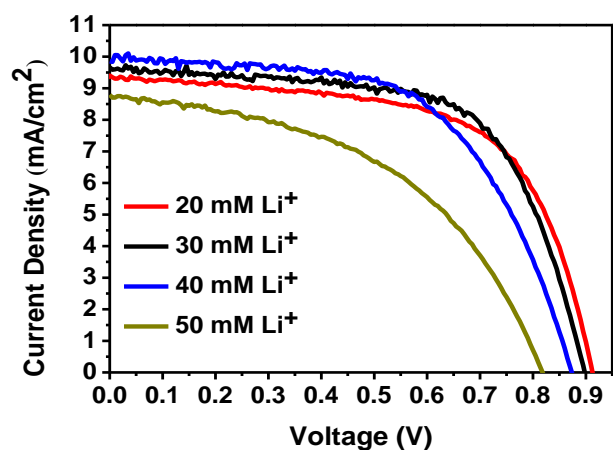


Figure S5. *J-V* curves with different concentrations of Li-TSFI for ssDSCs devices based on X3 and LEG4

Table S2. Influence of lithium salt on the photovoltaic performance parameters ^[a]

HTM	Li-TSFI	$J_{sc} / \text{mA cm}^{-2}$	V_{oc} / V	FF	η (%)
X3 ^[b]	20 mM	9.40	0.92	0.62	5.3
	30 mM	9.70	0.90	0.66	5.8
	40 mM	9.85	0.88	0.60	5.1
	50 mM	8.80	0.82	0.48	3.5

[a] 2.0 μm TiO_2 films and 100 $\text{mW}\cdot\text{cm}^{-2}$ simulated AM 1.5 G solar light. [b] 90 mM **X3** doped with 200 mM t-BP.

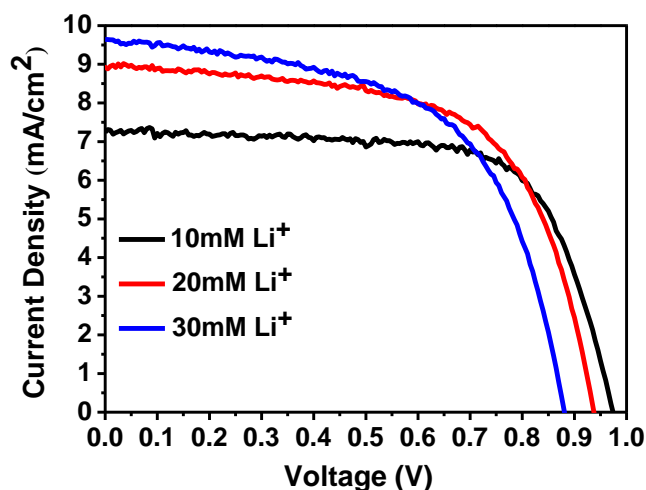


Figure S6. *J-V* curves with different concentrations of Li-TSFI for ssDSCs devices based on Spiro-OMeTAD and LEG4

Table S3. Influence of lithium salt on the photovoltaic performance parameters ^[a]

HTM	Li-TSFI	$J_{sc} / \text{mA cm}^{-2}$	V_{oc} / V	FF	η (%)
Spiro-OMeTAD ^[b]	10 mM	7.24	0.98	0.69	4.9

20 mM	8.90	0.94	0.65	5.4
30 mM	9.65	0.88	0.59	5.0

[a] 2.0 μm TiO_2 films and 100 $\text{mW}\cdot\text{cm}^{-2}$ simulated AM 1.5 G solar light. [b] 150 mM Spiro-OMeTAD doped with 200 mM t-BP.

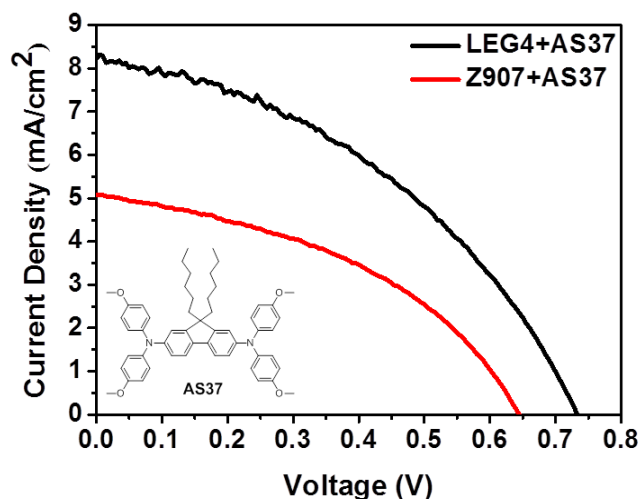


Figure S7. *J-V* curves for ssDSCs devices based on HTM AS37, dye LEG4 and Z907.

Table S4. The photovoltaic performance parameters for ssDSCs devices based on HTM AS37, dye LEG4 and Z907^[a]

HTM	dyes	$J_{sc} / \text{mA cm}^{-2}$	V_{oc} / V	FF	η (%)
AS37 ^[b]	LEG4	8.38	0.74	0.42	2.6
	Z907	5.10	0.65	0.43	1.4

[a] 2.0 μm TiO_2 films and 100 $\text{mW}\cdot\text{cm}^{-2}$ simulated AM 1.5 G solar light. [b] 304 mM doped with 18 mM Li-TSFI, 95 mM t-BP and 0.36 mol % tris(4-bromophenyl)aminium hexachloroantimonate (TBPA).^[5]

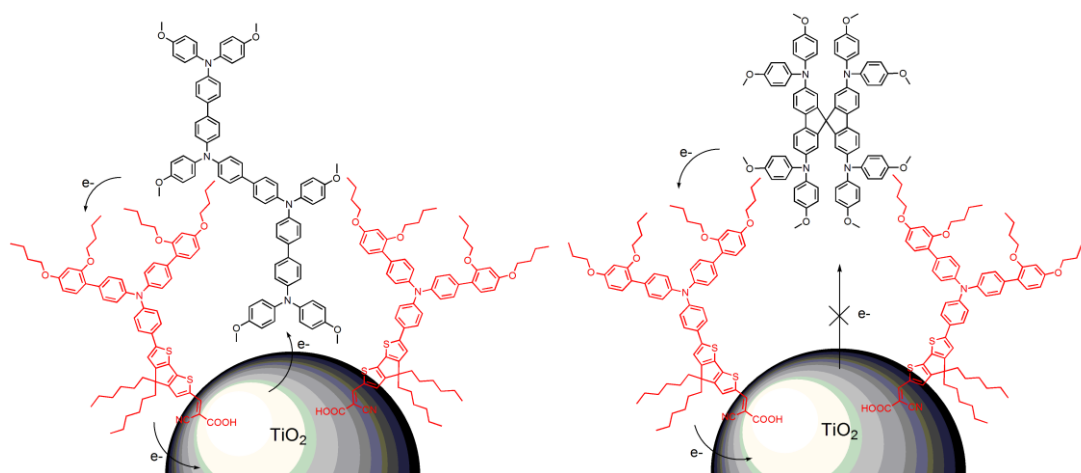


Figure S8. The schematic drawing of the situation of different HTMs on LEG4-sensitized TiO_2 surface.

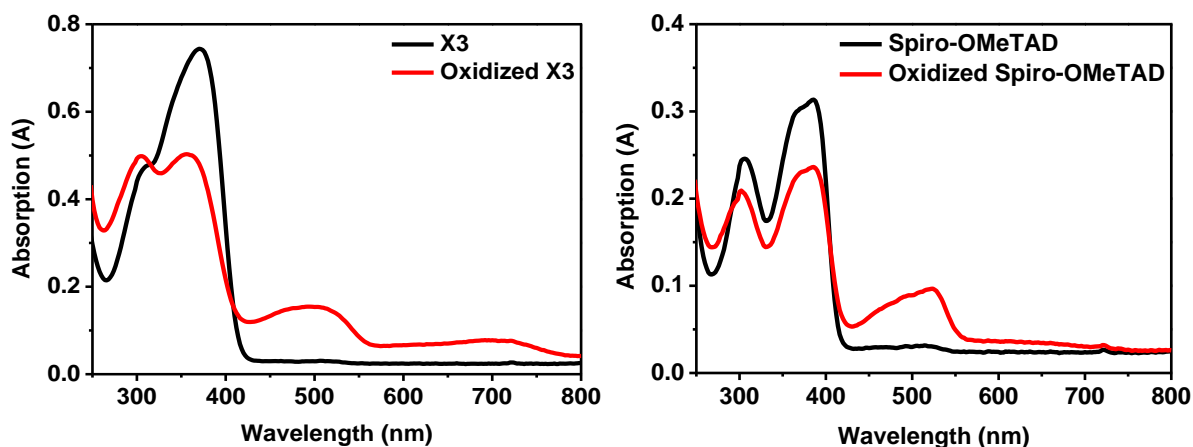


Figure S9. UV-Vis absorption spectra of HTMs and partly oxidized HTMs.

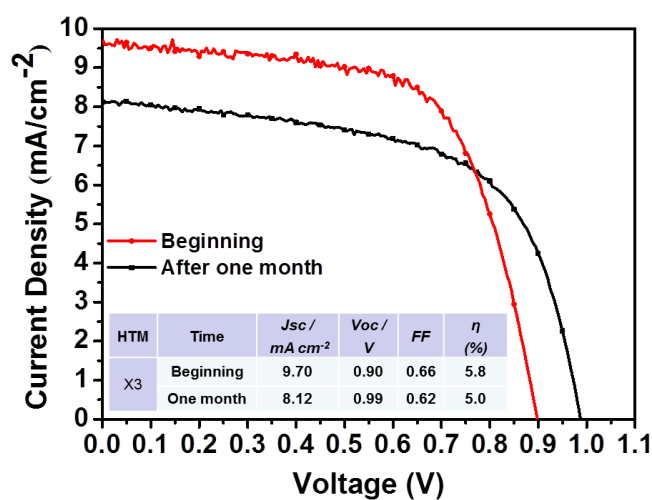


Figure S10. The J-V curves and photovoltaic data (inset) of fresh and aged (1 month, dark storage) LEG4 ssDSCs based on X3

References

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